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Characterization of thermochemically surface hardened titanium by light optical microscopy

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Keywords Titanium; Surface hardening; Mixed interstitial compound; Mixed interstitial solid solution; Oxidation; Carbo-oxidation; Metallography

Abstract

Thermochemically treated titanium grade 2 and 5 were investigated by light optical microscopy and hardness indentation. Gaseous oxidation in oxygen and N_2O containing atmospheres resulted in a diffusion zone of oxygen in solid solution in titanium with a hardness up to 1000HV. A surface scale consisting of oxide can be present depending on the treatment conditions. A new type of carbo-oxidation treatment was applied, where carbon and oxygen are simultaneously incorporated into the surface. This resulted in new microstructural features such as a deep zone of mixed interstitial solid solution, i.e. a diffusion zone, and surface regions consisting of a mixed interstitial compound (TiC_xO_{1-x} structure). Carbo-oxidation yields hardness values in excess of 2500 HV in the mixed interstitial compound and values up to 1500 HV in the diffusion zone. Simultaneously, with the surface hardening treatment, core hardening of the material can be obtained.

1. Introduction

Titanium and its alloys are used in applications where high specific strength and light weight are required, e.g. hardenable Ti alloys are widely applied in aerospace industry. Titanium is also known for its favorable corrosion properties, which are superior to most iron-based alloys and it is the material of choice for applications where high corrosion performance is required, e.g. off-shore, chemical industries etc. The favorable corrosion performance of titanium is a result of its ability to spontaneously form a strongly adherent surface oxide layer (self-passivation). Another aspect of titanium is its biocompatibility, making it the ideal choice for biomedical applications such as implants. However, titanium suffers from poor tribological properties making it unsuitable for applications where wear is experienced. The poor wear behavior strongly curtails more widespread use of this otherwise highly attractive engineering material. Surface hardening is one route to remedy this inherent problem of titanium

1.1. Surface hardening of titanium

Surface hardening of titanium is somewhat special due to the presence of the strongly adherent impenetrable oxide layer and that the element itself is a very strong nitride and carbide former. For this reason Ti is also extensively used as an *alloying element* in iron-based alloys. The impenetrability and strong affinity of the material itself to interstitials effectively excludes the use of conventional surface hardening methods for incorporation of nitrogen and/or carbon. In fact, the interstitial elements nitrogen, carbon and oxygen, are usually considered as impurity elements in Ti alloys. In order to circumvent the major problem with the passive layer barrier, relatively high temperatures are required and special processes have to be applied. A general overview of surface hardening methods based on oxygen, carbon, nitrogen and boron is given in references [1,2].

Gaseous nitriding at high temperature (e.g. 1000°C) is the “classical” way to surface harden titanium; exposing titanium to high purity molecular nitrogen gas at temperatures above, say 800°C, results in formation of TiN and Ti₂N nitride and a (supporting) diffusion zone with varying thickness [e.g. 3, 4, 5, 6]. The resulting surface layer of TiN has a golden color and will aesthetically change the appearance of the treated Ti, but will result in high hardness and low friction coefficient. More recently, attempts have been made to control the nitrogen-containing atmosphere to develop exclusively a nitrogen diffusion zone by applying a very low partial pressure of N₂ to avoid formation of Ti-nitrides [7]. There is limited work in the literature on carburizing of titanium [8,9,10,11,12]. Carburizing is carried out at high temperature in a carbon bearing gas (e.g. CH₄) and this transforms the surface into very hard cubic Ti_{1-x}C carbide. The solubility of carbon in titanium is low, which means that essentially no diffusion zone forms below the hard Ti_{1-x}C carbide. Hence carburizing results in a hard (thin) layer on a relatively soft substrate, which is typically unwanted due to risk of an egg-shell effect. Oxidation is generally considered as a detrimental high temperature corrosion mechanism, but in the case of titanium oxygen can – counterintuitively - be used for surface hardening. Titanium has a large capacity for oxygen in solid solution (32.4 at.%) and can form several types of oxides, e.g. rutile and anatase, TiO₂. In the 1960s oxidation of titanium and surface hardening with oxygen were investigated [13,14] and later also (sporadically) in different media, pressure- and temperature ranges [e.g. 15,16,17,18,19,20]. The oxygen-titanium system enables relatively thick diffusion zones due to the high solid solubility. A plethora of (mainly unsystematic) work on energy-assisted (plasma/ion-based) methods for incorporation of interstitials can also be found in the literature [e.g. 21,22,23 24,25]. The main benefit of such methods is the possibility to apply lower temperatures as sputtering is an integrated part of the method which effectively removes the barrier oxide layer.

So-called mixed interstitial compounds and solid solutions based on the ternary systems N-C-Ti, N-O-Ti, C-O-Ti are claimed to have interesting properties. These systems (viz. N-C-Ti) are also widely used for *coatings* by PVD/CVD methods. Thermochemical treatment applying two interstitials have been suggested to hold promise by Fedirko et al. due to the favorable properties that can be obtained [26,27]. The Ti system is particularly interesting as substitution of interstitial elements is possible between the oxides, nitrides and carbides; i.e. formation of a broad range of mixed-interstitial compounds or solid solutions [28]. The mixed-interstitial compounds and solid solutions have physicochemical properties significantly different from those of the binary compounds and solutions. The ternary compounds have higher hardness, wear resistance, corrosion resistance, thermal resistance and radiation resistance than the binary compounds [26]. In a recent publication on (largely uncontrolled) pack cementation treatment, which essentially is a gas process, Bailey and Sun showed that a network layer of TiC could be formed on top of a Ti(O) diffusion zone [29]. It was suggested that this (favorable) combination was the consequence of air oxidation during heating and subsequent formation of CO for carburizing at high temperature.

The present contribution shows the possibility for applying purely *gaseous processes* for controlled oxidation and transformation of the surface into mixed-interstitial solid solution and compound. It is not the intention to provide a systematic treatise of such processes but to showcase the possibilities of new (mixed-)interstitial gaseous surface hardening methods. Simultaneously with these treatments, core hardening can be achieved. In the following this is illustrated for titanium grade 2 and 5 by means of *light optical microscopy methods*.

2. Experimental

2.1. Materials

Titanium grade 2 and 5 were applied for the investigations and the nominal compositions of the materials are given in Table 1. Titanium grade 5 (Ti6Al4V) is an α/β alloy which typically is heat treated to obtain higher strength.

2.2. Gaseous surface hardening

Ambient air oxidation was carried out in a Nabertherm open box furnace. Atmosphere controlled O₂-Ar oxidation was carried out in an Entech furnace equipped with a Kanthal tube fitted with Brooks electronic mass-flow controllers. The total gas flow rate was 200 ml/min.

Carbo-oxidation was performed in a Netzsch thermal analyzer STA 449F1 in a carbon and oxygen providing atmosphere; the process is presently proprietary. The heating rate to process temperature was 20 K/min and the cooling rate was 50 K/min. The applied process temperatures were 1000°C and 1050°C. N₂O oxidation was also performed in the Netzsch thermal analyzer; total flow was 60 ml/min. Details about oxidation and carbo-oxidation treatments are provided in the figure captions.

3.3. Metallography

All treated samples were cut with a Struers precision Accutome. The cross sections were prepared by hot mounting in a Struers Prontopress 20 using Durofast resin. Preheating at 180°C for 5 minutes; holding time 6 min with 20 kN pressure and slow cooling (8 min). The embedded samples were prepared using a Struers Rotoforce 4 with Rotopol 22. The grinding and polishing procedure is given in table 2.

Etching was performed using Keller's reagent (185 ml distilled water + 5 ml nitric acid 65% + 3 ml hydrochloric acid 32% + 4 ml hydrofluoric 10%) for an etching time from 10 and 40 seconds, depending on the effect of the thermochemical treatment (microstructural features present).

Optical microscopy was performed on the cross sections using a Zeiss Neophot 32 reflected light microscope. Microhardness was measured using a Future Tech model FM-700 hardness tester on the mounted cross sections applying a load of 25 gf and a dwell time of 10s.

3. Results and discussion

3.1. Oxidation

Microstructures of oxidized titanium grade 2 are shown in Fig.1. Different treatments have been applied to illustrate the response of the material. Fig.1a depicts the microstructure after oxidation in a controlled O₂-Ar atmosphere at 750°C for 2 hours, combined with a post heat treatment for core hardening. At 750°C the high content of O₂ results in a fast development of a rutile TiO₂ scale and a shallow diffusion zone (not shown). The applied temperature of 750°C is below the beta-transus temperature and no transformation occurs in the sample, neither in the case nor in the core. Upon heat treatment at 970°C in ambient air the rutile layer is partly dissolved and the oxygen content in the surface is further augmented. The temperature 970°C is above beta transus for the material and the core is therefore fully transformed into b.c.c. β -Ti, while the oxygen-rich case remains h.c.p. α -Ti, as oxygen, in solid solution, is a strong alpha stabilizer. Final quenching in water has the consequence that the core is transformed into h.c.p. α' -martensite, possibly with some retained β -Ti. The oxide scale (viz. rutile TiO₂) present at 970°C spalls off during the quench treatment and leaves only the diffusion zone. The hardness of the core after quenching is 267 (\pm 17) HV compared to 202(\pm 33) HV for the delivered equiaxed condition. For low-alloyed Ti the maximum strength and hardness is obtained after quenching; tempering/ageing has a larger effect for alloyed Ti. The hardness of the case having an oxygen solid solution is 1050 HV at the surface. In Fig. 1B a comparable microstructure is observed, but the diffusion zone of oxygen is significantly thicker.

The treatment has been carried out solely in atmospheric air and was followed by direct quenching in water from the treatment temperature. A treatment temperature of 910°C is slightly above the beta transus and the core has transformed into martensite. The alpha-stabilized case (oxygen) clearly exhibits relatively large grains due to grain growth of the original alpha structure. The chemical nature of oxygen in solid solution is also evident; the etching response varies over the thickness of the diffusion zone, thus revealing a gradient in the dissolved oxygen content. The near-surface region of the oxygen-rich case appears unaffected by Keller's reagent, indicating improved corrosion resistance. The core microstructure shown in Fig. 1C is equivalent to the structure (and heat treatment) from Fig. 1A, except for a final aging treatment of the martensite, i.e. 600°C for two hours. For low alloyed Ti (as Grade 2) the strength/hardness is only marginally affected. However, some refinement of the martensite morphology is observed, i.e. more distinct packets and lamellas.

The microstructure shown in Fig. 1D is the result of a relatively long treatment at 1000°C (20 hours) in an atmosphere containing N₂O. N₂O is a very potent oxidizer similar to H₂O₂ (at lower temperatures). Indeed a thick oxide layer together with a thick diffusion zone is obtained. The core is transformed into a Widmanstätten structure, i.e. plates of α . The outer oxide layer has a layered morphology but no spallation is observed. The visual appearance of the treated sample was a milky-white surface which had swollen (clear change of dimensions). X-ray diffraction of the outermost surface of the oxide scale (not included) confirmed the presence of rutile TiO₂. The thick underlying diffusion zone is a consequence of the high temperature and long treatment time. Hardness values in excess of 1000HV were obtained in this zone. Massive grain growth is observed within the alpha-stabilized oxygen-rich case. Obviously, this treatment has no practical applicability but illustrates the behavior of Ti in a highly oxidizing atmosphere.

3.2. Carbo-oxidation

Carbo-oxidation as surface hardening treatment entails simultaneous incorporation of oxygen and carbon into the surface of the titanium. This can result in mixed-interstitial solid solutions or compounds (based on O and C), cf. the introduction. Fig. 2 depicts carbo-oxidation at 1000°C for 20 hours of Ti grade 2. The case consists of a mixed-interstitial solid solution zone (diffusion zone) and a mixed interstitial compound. The mixed interstitial compound phase is located preferentially along grain boundaries in the diffusion zone and as a relatively thin layer at the surface (cf. Fig. 2C). X-ray diffraction analysis (not included) revealed that the mixed interstitial compound is the cubic (B1) $\text{TiC}_x\text{O}_{1-x}$ structure. The hardness of the mixed interstitial compound phase is in average 1819(\pm 235) HV and the diffusion zone is up to 1148 HV. The morphology of the mixed-interstitial compound exhibits local gradients (cf. Fig 2C) and the center-line contains porosities or alternatively graphite precipitates (presently not confirmed). The overall layer thickness is approximately 400 μm , which is much larger than for single element hardening and strongly suggests a synergistic effect of dissolving two interstitials. The case can be considered a composite consisting of hard mixed interstitial compound phase ($\text{TiC}_x\text{O}_{1-x}$ type) embedded in a ‘softer’ diffusion zone. Indeed, preliminary results on wear in a tribometer using a pin on disc setup with an alumina counterpart (not shown) show very high wear resistance of the surface hardened Ti. Moreover corrosion testing (exposure in a solution containing 0.25 wt.% hydrofluoric acid adjusted to pH=1 with hydrochloric acid) showed that surface hardened Ti, similar to the treatment shown in Fig. 2, was inert even after 16 days exposure; the untreated Ti reference corroded immediately upon contact with the electrolyte.

The core of the surface hardened material is shown in Fig.3 and exhibits a Widmanstätten morphology (cf. above). The plates of alpha formed in the original beta structure are clearly seen. This results in a hardness increase compared to an equiaxed structure of alpha grains in the as-delivered condition.

A similar treatment, but at 1050°C, is shown in Fig. 4. Fig. 4a shows a macroscopic image (stereomicroscope) of the treated component. A uniform case of almost one mm is obtained both internally and externally. Clearly, the higher temperature results in faster growth. Figs. 4b to 4e show the morphology of the hard case at different magnifications. The same features in the mixed-interstitial compound as observed at 1000°C are visible, i.e. signs of porosity or graphite precipitation (Fig. 4E). It is clear that the mixed interstitial compound phase forms a network; at this temperature it is not fully clear if this is associated with the alpha grain boundaries. A hardness depth profile of the surface hardened zone is depicted in Fig.5. The figure contains two profiles: a profile obtained for the diffusion zone and one for the mixed-interstitial compound. The hardness of the mixed-interstitial compound phase is in the range 1700 to 3000 HV with an average around 2200 HV in the surface region which is significantly harder than the values obtained at 1000°C. This could indicate that more carbon is incorporated in the $\text{TiC}_x\text{O}_{1-x}$ structure. The large scatter of measured hardness values can be attributed to local hardness (composition) gradients in the mixed interstitial compound; here it also has to be emphasized that the values are obtained in a heterogeneous (3-dimensional) structure where measurement can be affected by adjacent (harder/softer) structures. The diffusion zone is generally harder than at 1000°C; a maximum of about 1500HV is obtained at a depth of 200 μm . The hardness drops slightly towards the surface but is compensated by a larger fraction of mixed-interstitial compound phase with a significantly higher hardness.

A feature which is evident is the incipient tendency for horizontal cracks in the diffusion zone (Fig. 4B). This is not surprising due to the very deep case depth achieved; certainly 20 hours at this treatment temperature is too much. The parallel and horizontal cracks suggest compressive surface stresses, which can be a combination of growth and thermal stresses.

In Fig. 6 surface hardened Ti alloy grade 5 is shown. The treatment temperature was 1000°C similar to Fig. 2 and 3. Clearly, the response of this alloys compared to (unalloyed) grade 2 is markedly different. In the near surface region a uniform layer can be observed, which is approximately 20 μm thick with a hardness of 1416 HV; this is most likely $\text{TiC}_x\text{O}_{1-x}$ rich in oxygen. Below this compound an approximately 100 μm thick diffusion zone extends and gradually fades into the core microstructure. This zone can be described as mainly oxygen-stabilized alpha. The presence of aluminum, also being a strong oxide former, is attributed to be responsible for the different response of the material. Preferential and fast formation of alumina (Al_2O_3) either as (dispersed) internal oxidation or as a thin surface zone can impede further growth. Al has a lower affinity to oxygen than Ti, but expectedly has a higher mobility than Ti in the alloy. Furthermore, the solubility product of Al_2O_3 is much lower than for TiO_2 . Hence it is expected that Al rich oxide is located at the surface where the oxygen pressure imposed by the gas atmosphere is highest. Indeed, for pure oxidation experiments the surface zone was rich in Al, as identified with EDS analysis (not shown). For the carbo-oxidation treatment the same behavior is expected and Al enrichment in the surface would impede fast ingress of carbon and oxygen. In this respect it should also be mentioned that Al does not form carbides. The role of vanadium, if any, is presently not clear. The core microstructure after cooling from 1000°C (50K/min) can be described as equiaxed primary alpha grains surrounded by (partly) transformed beta regions (acicular alpha in beta). This suggests that the material was treated in the two phase alpha-beta region (at 1000°C) prior to cooling.

3.3. Metallography and surface hardening of titanium.

Revealing microstructures in titanium alloys is not an easy task due to the superior corrosion resistance of these materials. This implies that relatively aggressive reagents have to be applied. The task is further complicated for surface hardened components where the surface region has a

different etching response than the core. For the present examples the incorporation of oxygen and carbon markedly changed the chemical behavior of the interstitial-rich part of the material.

The shown carbo-oxidation gaseous treatments appear highly effective in achieving deep hard cases on titanium (viz. unalloyed grade). This can be attributed to the synergistic effect of the two interstitial elements with respect to solubility and fast growth kinetics of mixed interstitial solid solutions and compounds. These topics are presently largely uninvestigated and will be addressed in future work.

4. Conclusions

Gaseous surface hardening of titanium grade 2 and 5 is possible by applying controlled oxidation or carbo-oxidation. Oxidation can result in a solid solution of oxygen in titanium which provides a strengthening effect. Hardness values up to 1000HV can be achieved. A new gaseous carbo-oxidation process enables very thick hard cases on titanium consisting of a diffusion zone with a hardness of more than 1200HV and a mixed interstitial compound zone with a hardness value of more than 2500HV. Case depths up to 1 mm can be obtained which imparts the treated surfaces with high wear and corrosion resistance. Different microstructural features (core and case) can be revealed by use of the metallographic procedures applied.

Tables:

Table 1. Nominal composition of ASTM Ti grade 2 and 5 (wt%).

Grade	Ti	Al	V	C	Fe	H	N	O
2	99.2	-	-	Max. 0.1	Max. 0.3	Max. 0.015	Max. 0.03	Max. 0.25
5 (Ti6Al4V)	90	6	4	-	Max. 0.25	-	-	Max. 0.2

Table 2. Metallographic preparation of titanium

Step	Grinding/polishing	Time [min]	Pressure (per sample) [N]
1	500 # paper	2.5	10
2	1000 # paper	2.5	10
3	4000 # paper	2.5	10
4	Mol 3 μm diamond suspension	3	10
5	Nap 1 μm diamond suspension	3	10
6	Chem, OPS (50% vol H_2O)	8	10

Figure captions:

Fig. 1. Ti grade 2. A) oxidation in 50 vol% O_2 at 750°C (2 hours) followed by slow cooling; then post heat treated at 970°C for 20 min. (air) and quenched in water. B) Oxidation in open air furnace (air) at 910°C for 2 hours and directly quenched in water. C) Core microstructure after heat treatment at 970°C for 20 min. and quenched in water (cf. A); then aged at 600°C for 2 hours. D)

Oxidation in 83%N₂O-17%Ar gas mixture at 1000°C for 20 hours followed by rapid cooling (50K/min).

Fig. 2. Ti grade 2. Carbo-oxidation at 1000°C for 20 hours. This results in formation of a case consisting of a mixed interstitial compound and diffusion zone. Different magnifications are shown.

Fig. 3. Ti Grade 2 core microstructure (same as Fig. 2) – different magnifications. Cooling rate 50K/min to RT.

Fig. 4. Ti grade 2. Carbo-oxidation at 1050°C for 20 hours. A) Stereomicroscopy - overview. All surfaces have been hardened – including the internal tread. B to E) Reflected light optical microscopy: Formation of a case consisting of a mixed interstitial compound and diffusion zone in the surface; different magnifications.

Figure 5. Hardness depth profiles for surface hardened Ti grade 2 (treatment shown in Fig. 4). Dotted lines are given to guide the eye (diffusion zone and compound zone). At 700 μm the compound zone ends.

Fig. 6. Ti grade 5. Carbo-oxidation at 1000 °C for 20 hours. A & B) Formation of a case consisting of a mixed-interstitial compound and a diffusion zone. C) Core microstructure (cooling 50K/min)

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FIG1

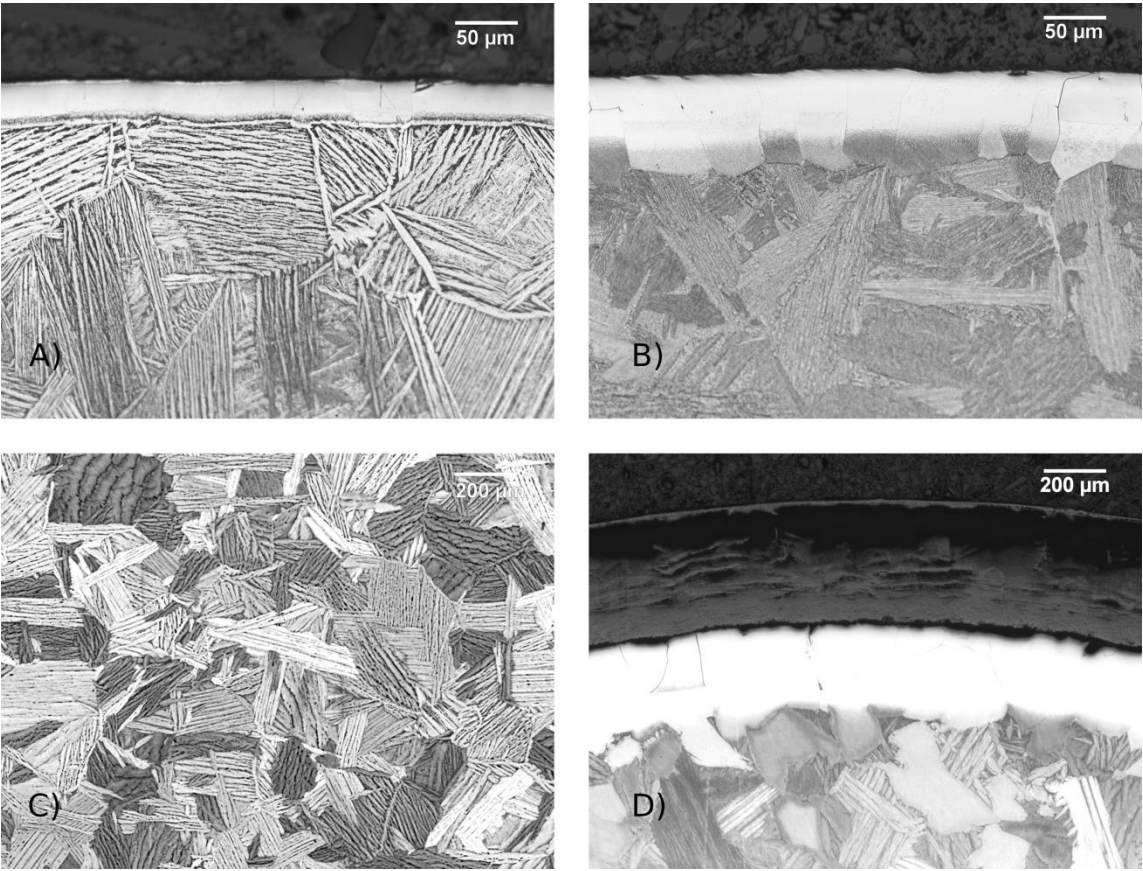


FIG2

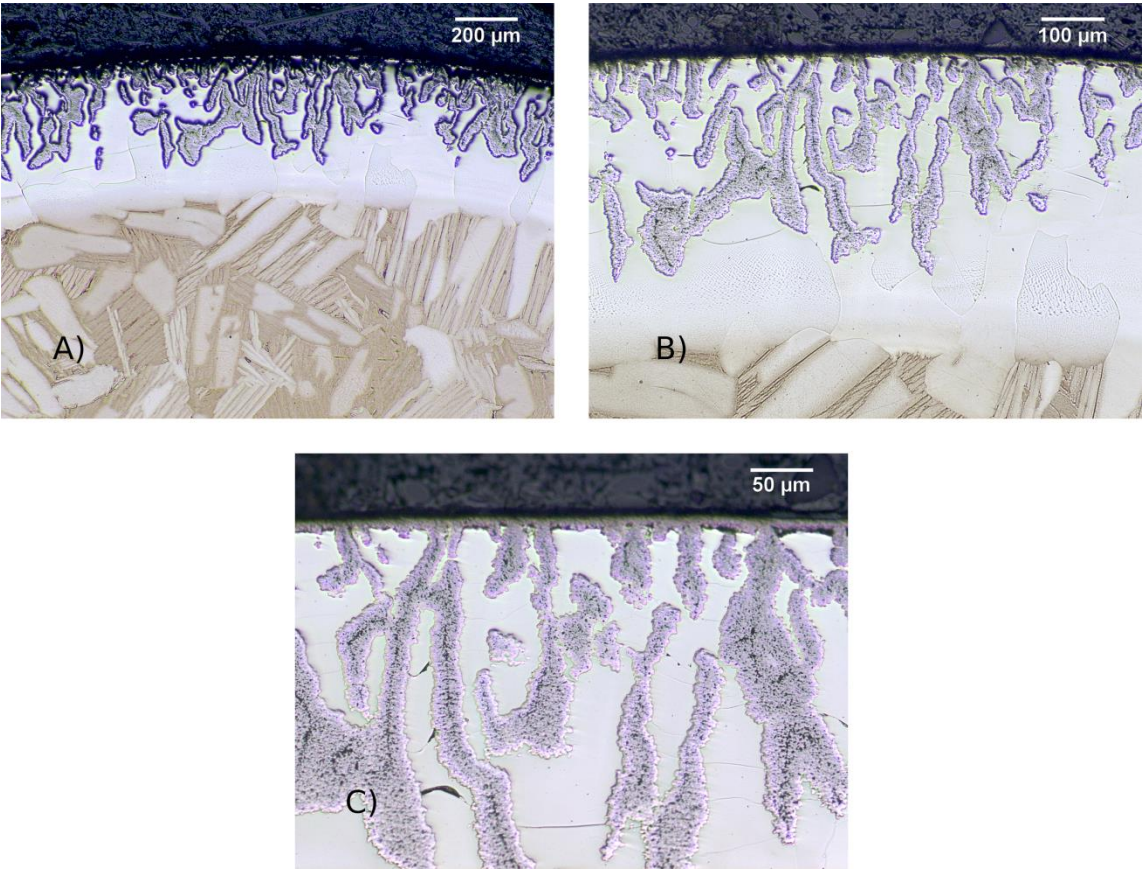


FIG3

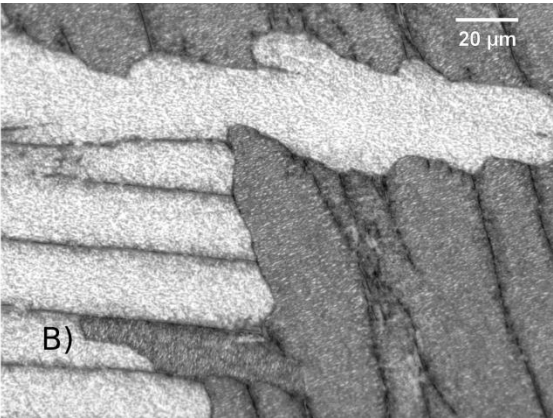
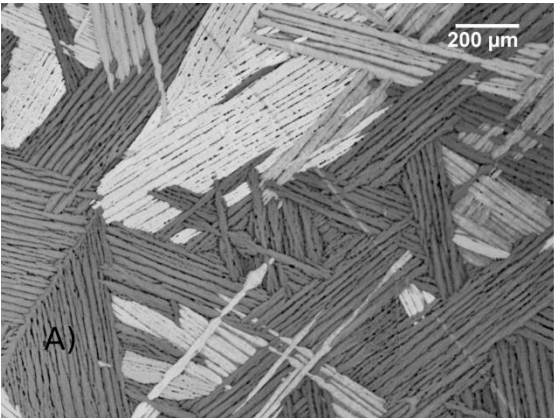


FIG4

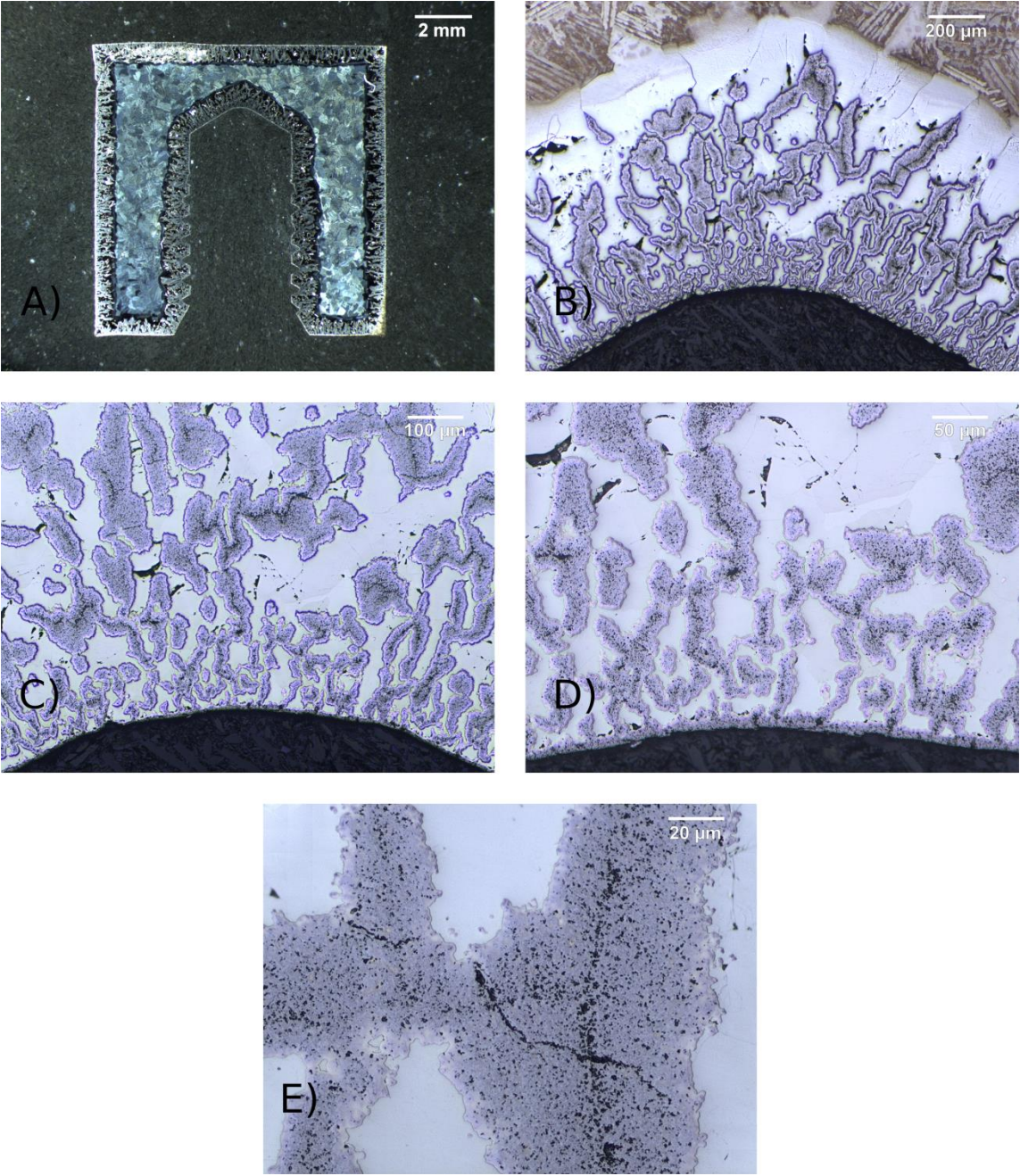


FIG5

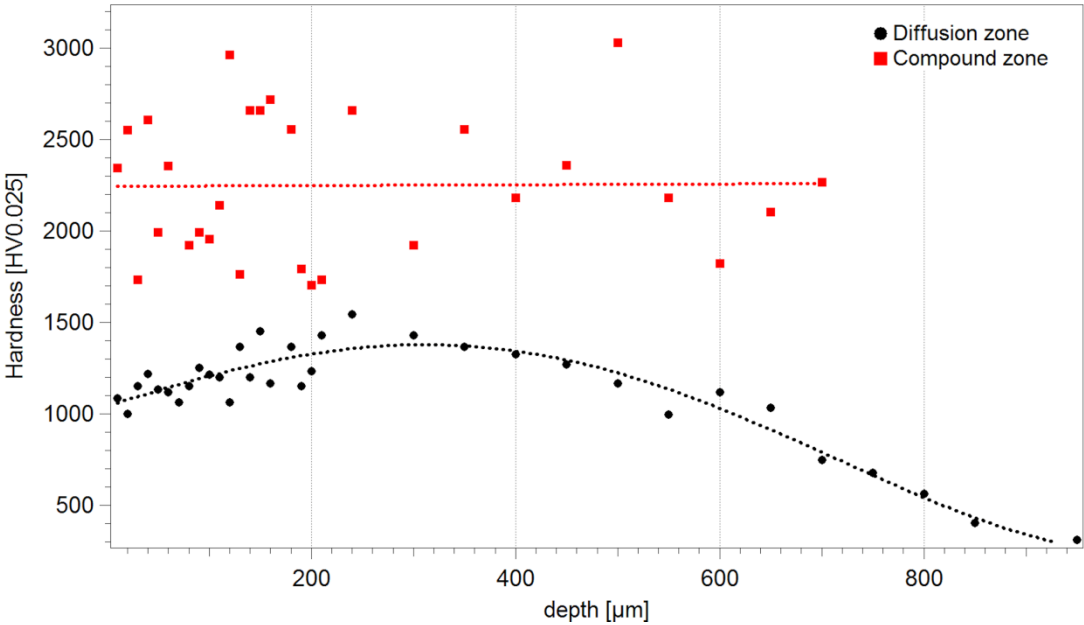


FIG6

